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AN ALTERNATIVE ANALYSIS OF NEW PARTICLE FORMATION: STUDYING THE MISFITS TO UNDERSTAND THE NORM

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Academic dissertation

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"We have in this fine dust a most beautiful illustration of how the little things in this world work great effects in virtue of their numbers"
J. Aitken, *On dust, fogs and clouds*, 1880[1]

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[1] On Dust, Fogs And Clouds, *Proceedings of Royal Society of Edinburgh* , XI, 1880 and *Transactions of Royal Society of Edinburgh*, 1880

An alternative analysis of new particle formation: studying the misfits to understand the norm

Stephany Nataly Buenrostro Mazon
University of Helsinki, 2019

"It is not, therefore, difficult to conceive how dusty particles may be formed in the great chemical laboratory of our atmosphere[2]".
C.S. Rafinesque, 1821

Abstract

In Finland, with each breath you are inhaling a luxury product: clean air. This is not the case for most people, as 90% of the human population lives within polluted air according to the World Health Organization. In addition to gas molecules, there are tiny solid or liquid particles floating in our air. We refer to this particle and gas mixture as an *aerosol*. Some aerosol particles are injected directly into the atmosphere from emissions like biomass burning or industries. The other half or more (~50-70%) are created in the air from precursor vapors in what is termed *new particle formation* (NPF) events. However aerosols are not only infamously involved in air quality, but play a major role in climate: they scatter incoming solar radiation, and indirectly affect climate by serving as the seeds that form clouds. In both cases, aerosols have an overall cooling effect, offsetting the global warming from greenhouse gases.

Yet aerosols and aerosol—cloud interactions have the largest uncertainty in our climate budget estimates. It is thus with urgency that we must concretize the sources, concentrations, and life-cycles of atmospheric particles around the world. However, while NPF events have been observed almost everywhere worldwide, global comparisons and quantification of NPF dynamics are mostly based on ideal, regional processes. As a result, a large fraction of field data is discarded from further analysis. In this thesis, we compared ideal NPF events to discarded, ambiguous or small-scale events in order to understand their potential contribution to aerosol dynamics and number concentrations.

We first determined the optimal ambient conditions for regional NPF in a boreal forest at SMEAR II station in Finland: clear-sky, sunny days, with low background aerosol concentrations, moderate temperatures, low relative humidity and high concentrations of oxidized organic vapors. We then reclassified the *undefined* days from 11 years of data (~40% of total data) to include transported/advected events and bursts of nucleation mode ions and particles that failed to grow to larger sizes. We consequently developed an automated classification scheme that accounts for both regional NPF events and the new classes of previously undefiend days. The result is a more robust analysis of NPF processes.

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[2] *Western Minerva, Or, American Annals of Knowledge and Literature*, edited by Constantine Samuel Rafinesque

We observed frequent nocturnal clustering in Hyytiälä (~30% of days from 11 years of data). Specifically, 1.5 to 2 nm ion concentrations were ~2 times higher at night than during daytime NPF events. However, this phenomenon disappears after ~3 nm cluster sizes. We conclude that a boreal nighttime forest is an effective source of sub-3 nm clusters that fail to grow.

Lastly, we compared nucleation mode aerosol at a pasture site and a rainforest site in the Amazon Basin, and present the first observations and characteristics of NPF commencing at ground level in the Amazon. No NPF occurred at the rainforest site. However, rain-enhanced intermediate ion bursts were frequent inside the forest canopy and raised ion concentrations by several orders of magnitude.

To get a global overview of NPF, it is understandable that we select unambiguous NPF cases of each region for inter-comparison. In this work, however, we focused on unconventional NPF-related features, with the thesis that omitting these events may lead to oversights of potentially relevant processes to NPF. We conclude that by investigating the less-than-ideal cases, we can find new mechanisms and sources that allow us to better understand, quantify and predict the processes that lead to the formation of new particles in the atmosphere.

Keywords: clusters, new particle formation, long-term field measurements, ions, aerosols, boreal, Amazon

Contents

List of publications

This thesis consists of an introductory section, followed by five research articles. **Papers I, II, III, V** published in the Atmospheric Chemistry and Physics journal are reproduced here under Creative Commons Attribution 3.0 License. **Paper IV** is reproduced with permission from the Boreal Environment Research Board.

I. Dada, L., Paasonen, P., Nieminen, T., **Buenrostro Mazon, S.,** Kontkanen, J., Peräkyla, O., Lehtipalo, K., Hussein, T., Petäja, T., Kerminen, V. M., Bäck, J., and Kulmala, M.: Long-term analysis of clear-sky new particle formation events and nonevents in Hyytiälä, *Atmos. Chem. Phys.*, 17, 6227-6241, doi: 10.5194/acp-17-6227-2017, 2017.

II. **Buenrostro Mazon, S.,** Riipinen, I., Schultz, D. M., Valtanen, M., Dal Maso, M., Sogacheva, L., Junninen, H., Nieminen, T., Kerminen, V.-K., and Kulmala, M.: Classifying previously undefined days from eleven years of aerosol-particle-size distribution data from the SMEAR II station, Hyytiälä, Finland, *Atmos. Chem. Phys*., 9, 667-676, doi.org/10.5194/acp-9-667-2009, 2009.

III. Dada, L., Chellapermal, R., **Buenrostro Mazon, S**., Paasonen, P., Lampilahti, J., Manninen, H. E., Junninen, H., Petäjä, T., Kerminen, V.-M., and Kulmala, M.: Refined classification and characterization of atmospheric new-particle formation events using air ions, *Atmos. Chem. Phys.,* 18, 17883-17893, doi.org/10.5194/acp-18-17883-2018, 2018.

IV. **Buenrostro Mazon S.,** Kontkanen J., Manninen H. E., Nieminen T., Kerminen V.-K. & Kulmala M.: A long-term comparison of nighttime cluster events and daytime ion formation in a boreal forest. *Boreal Env. Res*. 21: 242-261, 2016

V. Wimmer, D., **Buenrostro Mazon, S.,** Manninen, H. E., Kangasluoma, J., Franchin, A., Nieminen, T., Backman, J., Wang, J., Kuang, C., Krejci, R., Brito, J., Goncalves Morais, F., Martin, S. T., Artaxo, P., Kulmala, M., Kerminen, V.-M., and Petäjä, T.: Ground-based observation of clusters and nucleation-mode particles in the Amazon, *Atmos. Chem. Phys*., 18, 13245-13264, doi.org/10.5194/acp-18-13245-2018, 2018.

Term	Definition
Aerosol	A mixture of liquid and/or solid particles suspended in a gas. Atmospheric aerosols are such particles suspended in air.
Clusters	A nucleus of molecules bound together. Clusters can be electrically charged or neutral. They are continuously present in the atmosphere.
Condensation sink	The rate at which vapors condense onto pre-existing aerosol particles. An indication of the scavenging rate of condensable vapor concentration in the atmosphere. Unit: s^{-1}
Ion	An atom, molecule, molecular cluster or particle that carries an electric charge. In this thesis, *ions* mostly refer to a charged nanoparticle in the air.
Nucleation	When low-volatile vapors cluster to form a stable nucleus. Clusters undergo a constant competition between further growth and the breaking/evaporating off. If the conditions are favorable for further growth, the cluster can continue to grow in a new particle formation event.
New particle formation (NPF) event	An event when precursor vapors condense from the gas-phase into the particle-phase forming a nano-particle that may continue to grow into larger sizes for several hours.

1. Introduction

"A person leans back in an armchair, a thought floats through his mind: 'What is outside myself; what surrounds me?' Looking through the window, he sees the sun shining, clouds drifting by, smoke curling up from the nearby stacks, and sunrays passing through the window making dust particles dance – he sees aerosols."

Othmar Preining – Prologue to *History of Aerosol Science*, 1999, Vienna
Austrian Academy of Science, Clean Air Commission

With each breath, you are inhaling more than just air. In one respiratory cycle, you inhale approximately 500 cm^{-3} of air. And in every 1 cm^{-3} – an equivalent to a sugar cube – there are solid, liquid or mixed phase particles suspended amongst the atmospheric gases. We refer to this mixture as *aerosols*, and they are present all around the world. The number concentration of these aerosols differs by region, season, and size of the particles: A city like Helsinki, Finland, can have ~10,000 particles in 1 cm^3 of air (Aalto et al. 2005 at an urban background site). Take the same sugar cube to Shanghai or Delhi, and you may find 100,000 particles in the same space. Each breath, therefore results in millions of respired particles.

Aerosol science has been working to understand the sources, characteristics, distributions and dynamics of these particles in our atmosphere as early as the 1800's when scientists or philosophers where studying cloud and fog formation (e.g Aitken 1880). Already during these years of the Industrial Revolution aerosols where being linked to both climate and air quality. Studies have shown the detrimental effect of air pollution in the human respiratory and nervous system (Laden et al. 2006, Maher et al. 2016, Zhang et al. 2017, Shiraiwa et al. 2017, Kilian and Kitazawa 2018), the famous example being the death rates from the 1952 Great Smog of London (Wilkins 1954, Bell and Davis 2001, Hunt et al. 2003). On the other hand, aerosols could have a significant counter-effect to global warming (Andreae et al. 2005). They affect climate mainly though a negative radiative forcing (IPCC AR5 2013), contributing a cooling effect (total aerosol effective radiative forcing: -0.9 Wm^{-2}, range: -1.9 to -0.1 Wm^{-2}) that is counterbalancing the warming of the greenhouse gases (ERF: +2.83 Wm^{-2}, range: +2.26 to +3.40 Wm^{-2}). Aerosol particles interact with incoming solar radiation (direct climate effect; Bellouin et al. 2005) by mostly reflecting it off, with the exception of the absorbing aerosol black carbon (UNEP and WMO 2011, Yang et al. 2019). The indirect climatic effect is when aerosols act as the seeds that form clouds, either as *cloud condensation nuclei* (CCN) or *ice nuclei* (IN), and modify their properties such as cloud albedo, particle size, lifetime, heat budget and other

microphysical processes (Twomey 1991, Kerminen et al. 2012; Seinfeld et al. 2016). For the past decades, the Intergovernmental Panel on Climate Change (IPCC) has reported a compilation of studies that demonstrate the positive radiative forcing from greenhouse gases, particularly carbon dioxide (CO_2), in the Earth's radiation budget. However, the aerosol radiative component presents the largest uncertainty. The challenge lies in decreasing the uncertainties in the aerosol global budget distributions and in constraining the complex aerosol—cloud dynamics and future feedback responses arising from the change in climate (Merikanto et al. 2009; Yu and Luo 2009; Kulmala et al. 2011; Kerminen et al. 2012; Boucher et al. 2013; Myhre et al. 2013; Paasonen et al. 2013; Seinfeld et al. 2016; Zhao et al. 2017; Sullivan et al. 2018).

One challenge to determine the total aerosol budget is identifying the sources and the mass or number concentrations from each, for as many of the world's environments (eg. Paasonen et al. 2016). We can identify aerosols by the mechanism by which they are introduced into the air. Primary particles are ready-made particles injected into the air like wind picking up sand or dust, fauna releasing pollen or spores, waves breaking to release sea-salt, or emissions from biomass burning. Secondary particles, however, are formed in the air – *in situ* – when atmospheric gases condense to the particulate phase in what is referred to as new particle formation (NPF). Additionally, aerosols have both natural and anthropogenic sources. This distinction is particularly important in identifying and regulating human contribution to both climate change and air pollution, as anthropogenic emissions from fossil fuels (sulfur dioxide, SO_2, nitrogen oxides, NOx, organic compounds) and agriculture (NH_3) are directly involved in the productions of new particles (NPF), as will be discussed in the next section with more detail.

Aerosol particle properties are further defined by their diameter sizes, ranging from ~1 nm as in an initial cluster of molecules, to coarse particles of a few tens of micrometers in diameter like mineral dust and volcanic ash. Size segregation becomes important when discussing the aerosol lifetime (e.g. Williams et al. 2002), their interaction with solar radiation and cloud formation (e.g. ; Twomey 1991; McFiggans et al. 2006; Hand and Malm 2007; Yu and Luo 2009), or the health effects as they travel inside the human respiratory tract and blood stream (e.g. Donaldson et al. 1998; Meng et al. 2013).

Primary aerosol budgets include estimating the anthropogenic contribution of particles emitted from industrial and energy combustion sources. This includes identifying and constraining emission budgets for, e.g. road traffic, coal combustion and industrial

activities, from a local to a global scale (Paasonen et al. 2016). New particle formation presents a different challenge, given the diversity of precursor gases and meteorological conditions in the varied global environments in which they form (Kulmala et al. 2004, 2011; Dunne et al. 2016; Kerminen et al. 2018). Additionally, instrumentation capable of detecting particles and molecular clusters down to a couple of nanometers has only been available for the past couple of years (Tammet 2006; Mirme et al. 2007; Junninen et al. 2010; Vanhanen et al. 2011; Kulmala et al. 2012; Manninen et al. 2016) and is restricted to a few research groups. Yet NPF is observed around the world (Kulmala et al. 2004; Holmes 2007; Hirsikko et al. 2011; Nieminen et al. 2018; Kerminen et al. 2018), from the most remote, uninhabited places like Antarctica (Virkkula et al. 2009, Weller et al. 2015; Chen et al. 2017; Jokinen et al. 2017) and the free troposphere (Clarke 1993; Venzac et al. 2008; Takegawa et al. 2014; Rose et al. 2015, 2017; Bianchi et al. 2016), to the most particle-laden Megacities (Mönkkönen et al. 2005; Wu et al. 2007; Nie et al. 2014; Wang et al. 2016a; Wang et al. 2017; Qi et al. 2018; Yao et al. 2018; Chu et al. 2019). Most importantly, NPF is estimated to contribute substantially (~50-70%) to cloud condensation nuclei (Spracklen et al. 2006; Merikanto et al. 2009; Kulmala et al. 2016; Gordon et al. 2017). It is therefore imperative that we hone our understanding of the ingredients, pathways and budgets of newly formed particles in order to improve the aerosol component in future climate model scenarios.

The Station for Measuring Earth-Atmosphere Relations (SMEAR-II) in Hyytiälä, Finland (Hari and Kulmala 2005) has given us the unique opportunity to study long-term trends of aerosols, new particle formation, and clean environmental conditions that produce them (Nieminen et al. 2014; **Paper I-V**). This is important for two reasons:

(1) the Boreal biome is the largest single biome covering the span of North America, northern Europe and northern Asia. Hence, it is important to characterize the aerosol loading and cloud seeding of a boreal forest, particularly to understand the response of a boreal forest to climate change (Tunved et al. 2006, Spracklen et al. 2008; Kulmala et al. 2014; Hede et al. 2015; Ellison et al. 2017).

(2) It provides the longest aerosol measurement data set available, complemented with numerous environmental/meteorological parameters that allow for the most complete analysis of NPF events (e.g. Laakso et al. 2004; Hyvönen et al. 2005; Yli-Juuti et al. 2011; Nieminen et al. 2014; Petäjä et al. 2016; Zaidan et al. 2018; **Paper I, II**).

Nonetheless, the SMEAR-II dataset, as in other world datasets, have resulted in a large number of "undefined days" (40%, **Paper II**), which removes a large fraction of the data from further analysis. Furthermore, NPF analyses have focused on daytime hours, according to the conventional NPF event classification system by Dal Maso et al. (2005), again, restricting the analysis of atmospheric processes to conventional regional NPF events and omitting what may be happening outside this time window (**Paper II, III, IV**). Additionally, observations from ground stations are taken to represent the processes and characteristics of the region. The atmospheric boundary layer (BL) is dynamic (Blackadar 1957; Stull 1988), however, so what we observe at ground level may not be representative of what is happening meters above or further out horizontally (**Paper II, V**). The concern for spatial representativeness of the observations can be addressed by comparing ground-to-tower (Du et al. 2017; Zha et al. 2018; Zhou et al. 2018), airborne (Leino et al. 2019), or as a set of neighboring stations (Vana et al. 2016; Berland et al. 2017; Carnerero et al. 2018).

Ultimately, research has highlighted the competitive process of NPF under various possible chemical and nucleation pathways. This thesis looks at events that do not comply with or are overlooked from the established classification of an NPF event, in an effort to identify and highlight less prominent mechanisms that could ultimately be relevant in the understanding of particle formation process. This work uses decadal-long field observations from SMEAR II station in Finland (**Paper I-IV**), and compares long-term and campaign observations at the only region in the world where NPF has not been previously observed at ground level: the Amazon Basin (**Paper V**).

In summary, the aims of this thesis are:

1) to identify the most favorable ambient conditions for NPF events using a long-term aerosol dataset (**Paper I**) to serve as a reference in comparison to days with less-than-ideal NPF conditions, including *undefined* days (**Paper II, III**), non-regional NPF (**Paper II, V**), and night-time clustering (**Paper IV**),
2) to increase the robustness of NPF data analysis (**Paper II, III**) from the conventional classification system of Dal Maso et al. (2005), and include sub-3 nm sizes in the classification,
3) and to assess the spatial-variability of nucleation mode aerosols between a rainforest canopy and an open grassland within the Amazonian boundary layer (**Paper V**).

2. New particle formation

2.1. Introducing new particles in the air

In an ideal case, we would be able to quantify the total global aerosol budget, to identify the sources and sinks of particles, and to understand their life evolution as they grow and age. We would be able to model the interaction of aerosols and clouds in past scenarios to understand how the start of human industrial and agricultural activities have contributed to the present climate, and in doing so project how it may be in future scenarios. In the ideal case described above, we would have managed to understand and quantify the mechanisms that form new particles under our world's varied environments.

However, there remain questions that require answers at all scales, from identifying the reaction pathways of gas-phase precursors to particle-phase aerosols (Kroll and Seinfield 2008; Hallquist et al. 2009; Jokinen et al. 2015), to the fraction and composition of new aerosols that reach CCN sizes (Weber et al. 2007; Yu and Luo 2009; Merikanto et al. 2009; Kerminen et al. 2012; Paasonen et al. 2013; Yu et al. 2014; Petäjä et al. 2016; Gordon et al. 2017; Zhao et al. 2017; Sullivan et al. 2018; Schmale et al. 2018), and the influences that these CCN have on cloud properties. For this reason, aerosol science puts great effort in elucidating the mechanisms behind NPF, by gathering field observations, laboratory experiments and model simulations in a global research community.

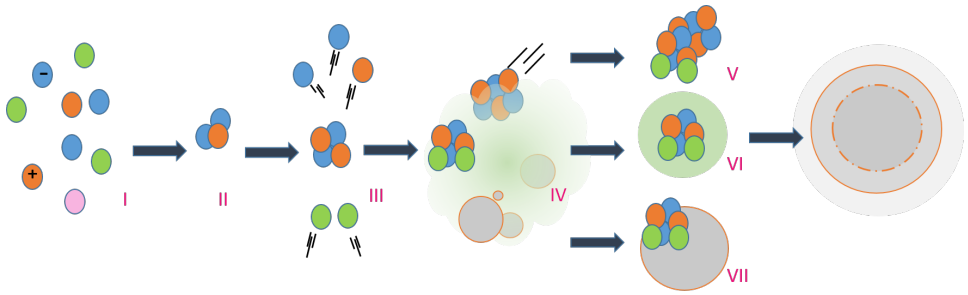

Figure 1: New particle formation: (I-II) molecular neutral and charged clusters undergo (III) condensation and evaporation constantly, until the right conditions allow the cluster to overcome losses and (IV) nucleate into a particle that continues (V-VI) to grow or (VII) is lost to a larger pre-existing particle.

This is what we know so far (Fig.1). New particles form at ambient conditions around the world when (i) precursor vapors in the atmosphere first form (ii) molecular clusters. (iii) These initial clusters are observed worldwide and they are almost constantly present

(Kulmala et al. 2007, 2011; Kontkanen et al. 2017), illustrating an ongoing balanced process of condensation and evaporation – or clustering and breaking off – of both charged and neutral clusters (Kulmala et al. 2007, 2013). In the next stage, (IV) the stabilized nucleated cluster can grow as a particle via (V) self-coagulation, (VI) further condensational growth, or be lost (VII) scavenged by larger pre-existing particles or via deposition. What forms stable clusters? A certain combination of molecules, with the strongest bonding, the right stereochemistry, perhaps a charge?

It has been shown that sulfuric acid is the main component for nucleating clusters in most environments (Weber et al. 1996; Birmili et al. 2003; Kulmala et al. 2004; Berndt et al. 2005; Sipilä et al. 2010; Zhang et al. 2011), but a binary nucleation of sulfuric acid with ambient water vapor is not enough to explain the rates and growth of new particle formation observed under the boundary layer atmospheric conditions. Cluster models (Kurtén et al. 2007; Merikanto et al. 2007; Ortega et al. 2012a), laboratory experiments (Ball et al. 1999; Kirkby et al. 2011; Almeida et al. 2013; Bianchi et al. 2014) and field observations (Schobesberger et al. 2013, 2015; Hodshire et al. 2016; Bianchi et al. 2017) have indicated that the introduction of bases like ammonia and, more efficiently, amines can stabilize the sulfuric acid in an acid-base ternary nucleation in the most favorable mechanism in the tropospheric boundary layer. Additionally, volatile organic compounds (VOCs) can transform into participant precoursor vapours when they oxidize into highly oxygenated organic molecules (HOMs) (Donahue et al. 2005; Ortega et al 2012a; Ehn et al. 2012, 2014; Jokinen et al 2015; Kretschmer et al., 2015; Tröstl et al. 2016; Ng et al. 2017; Bianchi et al. 2019). HOMs have been shown to cluster under various environments with sulfuric acid (Riipinen et al. 2007; Petäjä et al. 2009; Metzger et al. 2010, Kulmala et al. 2013; Vakkari et al. 2015; Jokinen et al. 2017), amines and ammonia (Kirkby et al. 2011; Riccobono et al. 2014; Jokinen et al. 2018), iodic acid (Sippilä et al. 2016), or with themselves in purely biogenic clusters stabilized by an ion-induced nucleation pathway (Kirkby et al. 2016, Bianchi et al. 2017, Rose et al. 2018). But, not surprisingly, concentrations of vapors differ across environments, latitudes, seasons, and even time of day. For example, coastal NPF has been shown to occur via the abundant iodine species, and not sulfuric acid (Sipilä et al. 2016).

Lastly, it is important to dedicate some words specifically to ions, the sources of their charges and the role of charge in NPF. In addition, because ion spectrometers (**Papers I, III-V**) and mass spectrometers detect ions to study the earliest stages of clustering and

nucleation, we must keep in mind what it is we are measuring. Small air ions are formed mainly when ionizing radiation like radioactive radon and gamma or cosmic rays impact an air molecule (N_2, O_2), turning it into a *primary ion* (Israël 1971). Less ubiquitous, single events involving water droplets like rain or waterfalls (Hirsikko et al. 2007; Tammet et al. 2009; **Paper V**), high winds or thunderstorms (Hirsikko et al. 2007; Chen et al. 2016), or even engines and exhaust tube (Yu and Turco 1997; Lähde et al. 2009) can form ions. These primary ions can transfer their charge to trace gases, clusters or pre-existing particles (Laakso et al. 2007; Hirsikko et al. 2011; Chen et al. 2016), thereby producing charged aerosol precursor molecules, ion clusters or charged aerosols. In turn, these secondary ions can continue growth via condensation, ion—neutral attachment or ion—ion recombination (neutralizing their charge) (see ion formation rate eqn in Methods). The contribution of ions to the formation of new particles is considered to be small compared with neutral pathways in the boundary layer (Iida et al. 2006; Boy et al. 2008; Manninen et al. 2009; Kulmala et al. 2013; Schoebesberg et al. 2015; Dunne et al 2016). However, a charge can provide a stabilizing effect for the nucleating cluster and enhance the formation of new particles in what is termed *ion-induced* NPF (Enghoff and Svensmark 2008; Zhang et al. 2011). For example, studies have shown the stabilizing effect of charge on binary water-sulfuric acid clusters (Ricobbono et al 2014; Schobesberg et al. 2015; Duplissy et al. 2016) under elevated ion, sulfuric acid and relative humidity values, and low concentrations of alternative vapors (e.g higher troposphere, Yu and Turco 2000; Froy and Lovejoy 2003; Arnold 2006); or in pure biogenic nucleation where HOMs clustering is not outcompeted by neutrals (Kirkby et al. 2016; Rose et al. 2018).

Specifically, studies have shown that ions may be more important at the clustering stage (Wilker et al. 2008; Schobesberg et al. 2015; Rose et al. 2018; Yan et al. 2018; **Paper IV**), where negative polarity may even be most preferred over positive polarity (Wilhem et al. 2004; Iida et al. 2006). Neutral pathways would then dominate the nucleation stage, particularly beyond 2 nm diameters. It is important to note that while *ion-induced* nucleation (IIN) considers clusters that remained ions (keep the charge) during the nucleation process, the term *ion-mediated* nucleation (IMN) includes both charged clusters and neutral clusters formed through ion-ion recombination (where they consequently lose their charged state).

So on one hand the atmosphere has an oxidative capacity, responsible for lowering the vapor pressures of precursor vapors allowing them condense more readily. On the other, it

has an ionization capacity, introducing charges that will be picked up by the most willing compounds (proton affinity).

2.2. What to look for in aerosol data: classifying NPF events

If a cluster pool is ever present, why would new particle formation not occur constantly, at all hours and all conditions? Looking at the various ambient conditions and different stages involved in new particle formation, we can appreciate that NPF is a competition of chemistry –of oxidation products or nucleation pathways– enhanced or truncated by the environmental conditions that, when favorable, push forward the survival of the smallest clusters to sizes of ~2 nm and beyond (Riipinen et al. 2007; Kulmala et al. 2013, 2014; Schobesberg et al. 2015).

In order to couple the chemistry and ambient conditions with the physical observations of new particle formation from field measurements, we first distinguish between the days when new particles are being formed (*NPF event* days) and the days with no NPF (*nonevent* day) by following a visual classification proposed by Dal Maso et al. (2005) (see Fig. 2 for examples of the Dal Maso et al. 2005 classes). An aerosol number-size distribution surface plot of a single day is visually inspected and its features are evaluated against the guidelines specified by the Dal Maso et al. (2005) classification (see Kulmala et al. 2012). In general terms, a new mode of nucleation mode particles (<25 nm) must appear and show a continuous growth into larger sizes, for the duration of >1 hr, forming a shape colloquially referred to as an NPF 'banana'. Days that clearly do not show a new nucleation mode are labelled *nonevents*, and it is assumed no particle formation is occurring. Ambiguous days where nucleation mode particles might intermittently appear, show no growth, or first appear in a mode >20 nm, are labelled as '*undefined days*' and are normally discarded from further analysis. In this thesis, we analyze the undefined days in **Papers II** and **III.**

We must note that the Dal Maso et al. (2005) classification was built using a mobility spectrometer instrument with a cut off size at 3 nm. Later on, Kulmala et al. (2013) confirmed the presence of the "cluster band" of ~2 nm neutral particles and ions constantly present in the atmosphere (see Fig.1). Therefore, an ideal number-size distribution plot showcasing an NPF event will consist of a constant cluster band <2 nm and a morning banana growing in size until the late evening or even the next morning.

Employing a common protocol for the classification and definition of regional NPF (Dal Maso et al 2005; Kulmala et al. 2012) gives coherence to global new particle formation research (e.g. Nieminen et al. 2018). Even so, some datasets around the world have shown particular features. For example, sudden bursts of nucleation mode aerosols termed 'apple' events are reported in coastal Ireland (Vana et al. 2008) and Northern Greenland (Dall'Osto et al. 2018); "shrinking bananas" have been observed in urban sites (Hong Kong: Yao et al. 2010; Mediterranean: Cusack et al. 2013; Madrid: Alonso-Blanco et al. 2017, Carnerero et al. 2018); transported events seen as the second half of a 'banana' plot (Cai et al. 2018; **Paper II**), or bursts of small or intermediate ions resulting from precipitation or wind such as "rain events" (Hirsikko et al. 2007; Vana et al. 2008; Tammet et al. 2009; Buenrostro Mazon in prep., **Paper V**). Hirsikko et al. (2007) extended the NPF classification to include sub-3 nm ion bursts using ion spectrometer data with a cut-off size down to ~1 nm that would otherwise have been unaccounted for under the traditional NPF classification. **Papers II** and **III** propose additional classifications to expand the case studies analysis beyond regional and ideal NPF events (see section 4).

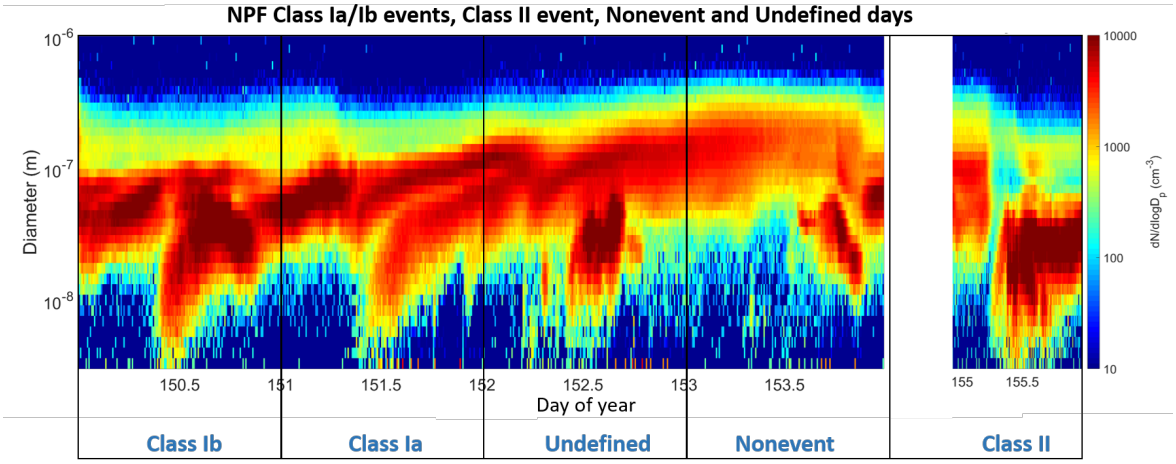

Figure 2: Example days following the new particle formation event classification by Dal Maso et al. (2005). Class Ia/Ib events, Class II event, nonevent and undefined day for the week 30 May – 04 June 2018.

2.3. A puzzle of chemistry and meteorology: characteristics of NPF event days

The long-term comprehensive dataset from SMEAR II, Finland (see Methods), has allowed for data mining techniques to identify predictive parameters of NPF events (Hyvönen et al. 2005; Mikkonen et al. 2006; Zaidan et al. 2018; Paper III) resulting, for example, in a successful NPF forecast by Nieminen et al. (2015) a couple of days prior to the event based on air mass trajectories and meteorology. Yet at a global scale, environments are too varied and fieldwork has not fully represented all regions of the world, with a concentration of measurement stations in certain regions such as Europe (Kulmala et al. 2004, 2011, Manninen et al. 2010; Kerminen et al. 2018; Fig. 3). Nonetheless, there are certain prevailing characteristics that emerge from global NPF studies, which we will now discuss.

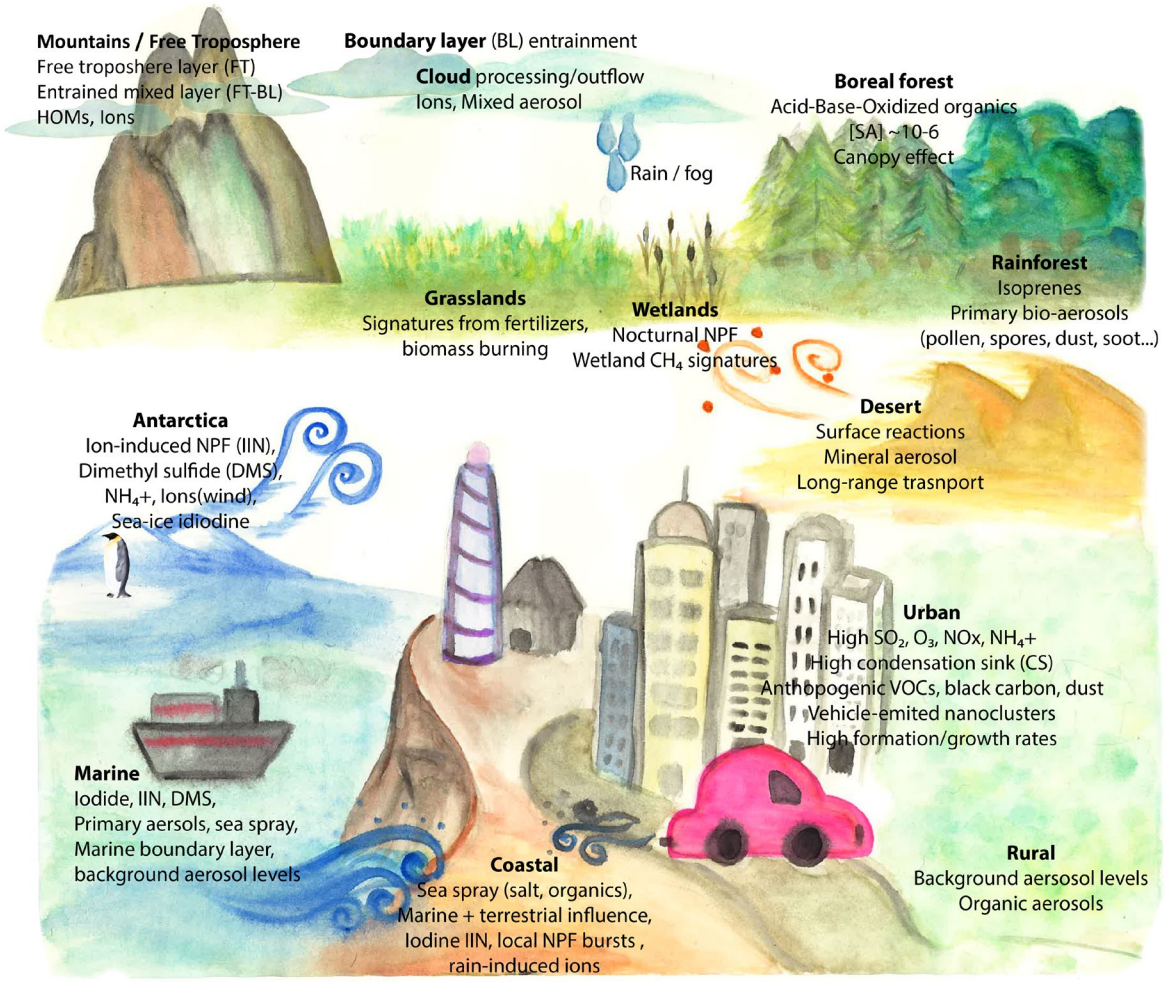

Figure 3: New particle formation has been observed around the world. Different pathways and main chemical clustering compounds have been reported in various environments around the world.

Solar radiation is a key component of NPF indicated by the amount of UV radiation or by the level of 'cloudiness'/clear sky, (e.g. Jokinen et al. 2018) which can separate NPF events from nonevents. This points to the photochemical oxidation needed in the formation of sulfuric acid and certain HOMs from precursor vapors. Both low *relative humidity* (RH) and low *condensation sink* (CS) are linked to NPF (Birmili and Wiedensohler 2000; Hyvönen et al. 2005; Nieminen et al. 2014; **Paper I-II & III**). Condensation sink refers to the loss term of condensable vapors onto the surfaces of pre-existing particles, so low values indicate low background aerosol concentrations. Clean air favors NPF in most regions but we must note that high CS in highly polluted megacities does not completely deter NPF (e.g. Mikkonen et al. 2006; Hamed et al. 2007; Nie et al. 2014; Kulmala et al. 2017; Yao et al. 2018); rather different particle dynamics (Kulmala et al. in prep) or the source and concentrations of vapors (Qi et al. 2018) could outdo the NPF-inhibiting effect of CS. Related parameters like *wind directions* and *back trajectories* are linked to the fact that air originating from clean sectors favor NPF (eg. north-west Arctic sea sector in the case of Hyytiälä, Finland) (e.g. Sogacheva et al. 2008, **Paper II**), or indicate time spent over a certain terrain like forest or open sea collecting precursor vapours (Tunved et al. 2006; Väänänen et al. 2013). Boundary layer (BL) dynamics, particularly *turbulence*, has been linked to NPF onset or advection from higher altitude (e.g. Nilsson et al. 2001; Gröss et al. 2018). It can serve as a mechanism to get together the right ingredients (Mogensen et al. 2015) and environmental conditions, as in the case of BL and free troposphere (FT) interface (Rose et al. 2015) or to segregate polluting unfavorable conditions (Bianchi et al. 2016). An overview of chemistry can be seen from trace gas concentrations such O_3, NO_x, SO_2, and organics (or their proxies) and are common indicators and predictors of NPF (Mikkonen et al. 2006; Nieminen et al. 2014; Zaidan et al. 2018; and **Papers II & IV**).

The importance of each parameter is far from trivial, however (eg. Nilsson et al. 2001, Mikkonen et al. 2011, Zaidan et al. 2018). The effect or the change in value of one parameter can implicate a change in meteorology or a change at a molecular level, and it is not straightforward to single one out. For example, we have asked ourselves if a cluster band is always present, why nucleation is not ongoing. A cluster will form and break until it is stabilized and growth is favored, following energetic hierarchies at a molecular level —such as chemical pathways, associated collision rates, a change in vapor pressures— or at larger scale changes such as the availability of precursor VOC vapors. The ambient

relative humidity is associated with cloudiness, and thereby with intensity of incoming solar radiation, but it also determines the amount of water vapor that can be involved in clustering. On top of this, these parameters are also dependent on each other, as can be seen for example with a change of season or diurnal cycles (eg. Crippa and Pryor 2013; Salma et al. 2019). For example, an atmosphere at sea level versus high elevation site would differ with respect to their overall ionization capacity, T, RH, sources of trace gases and background aerosol. Each parameter, with its individual variability (diurnal, seasonal, etc.), in turn affects the others. In the real atmosphere, the challenge is trying to understand what conditions favor one particle formation mechanism over another, so that our nucleation parameterizations become more representative in quantifying both regional and global NPF budgets. Bringing field observations together from around the world, replicating them in chambers and trying to put the puzzle together is what makes this so exciting.

3. Methods

3.1. Measurement sites

Figure 4: Map of stations. Left: Stations T0t and T3 in the Amazonia State, Brasil. Right: SMEAR II station in Hyytiälä, Finland.

3.1.1. SMEAR II, Hyytiälä, Finland

The Station for Measuring Ecosystem–Atmosphere Relations (SMEAR) II is located in Hyytiälä, southern Finland (61°51’ N, 24°17’E; 181 m above sea level; Hari and Kulmala 2005; Fig. 4 right panel). SMEAR II is a background station located within a ~60 year old boreal pine forest, in a pristine rural environment ~60 km NE from the nearest urban city of Tampere and ~200 km from the capital city Helsinki. It is a boreal forest site embedded in a homogenous Scots pine forest (*Pinus Sylvestris*). The SMEAR II station is the flagship for the Global SMEAR model of networking stations (Kulmala 2018), continuously measuring soil – forest—atmosphere processes and interactions. The comprehensive measurements surpass 2,000 parameters of biogeochemical fluxes, micrometeorology, aerosol and atmospheric chemistry. It has the world’s longest continuous measurements of aerosol number-size distribution concentrations beginning from 1996 until now. SMEAR II has pioneered in the integration of the latest instruments in the world, the latest of which include the atmospheric-pressure-interface time-of-flight mass spectrometers (Junninen et al. 2010; Jokinen et al. 2012) that enabled the detection of gas-phase oxidized molecules (naturally charged: API-ToF; and for charging and detecting neutral molecules: CI-API-ToF) and finally bridge the gap between the gas precursors and particulate phase aerosols. The SMEAR II station serves as a model monitoring station for upcoming stations around the world.

3.1.2. The Amazon, Brazil

We compared two sites at the Brazilian Amazonia, namely a rainforest site and an open grassland (Fig. 4 left panel). Our measurements included a long-term dataset of the Amazon rainforest (September 2011 to January 2014). The measurement campaign data presented in this thesis covers two Intensive Observational Periods (IOP) (Martin et al. 2016, 2017) during the wet and dry season of 2014 at an open grassland site near Manacapuru, Brasil.

T0t site – inside the rainforest: The T0t site inside the rainforest canopy is considered an ecological reserve (Martin et al. 2010). It is located 60 km north of the Amazonian city of Manaus in northern Brazil (2.609°S, 60.2092°W). The T3 instrumentation was located in a measuring hut surrounded by dense rainforest with a homogeneous canopy on average 30 m high.

T3 – open pasture site: The open pasture T3 site located 70 km downwind of the city of Manaus (3.2133°S, 60.5987°W) was part of the ARM Mobile Aerosol Observing System (MAOS; Mather and Voyles 2013). The site intersects a pollution plume from Manaus regularly. When the wind direction changes, the T3 site can be considered a pristine continental site. Measurements at this site were sampled at 2 meters above ground level.

3.2. Instrumentation

3.2.1. Air ions and aerosol particles

The main analysis of **Papers I-IV** are based on the number size distribution of total aerosols and ions using ion spectrometers. The main component of the ion spectrometers is the differential mobility analyser (DMA; Hewitt 1957; Winklmayr et al. 1991; Mirme et al. 2010) that classifies particle size by differentiating their electrical mobility within an electric field into a corresponding electrometer detector. The electric signal counts and the particle's corresponding electrical mobility are then converted to mobility-equivalent) and number concentration. The voltage changes to a scanning mode to cover the size range of the instrument.

Neutral Air Ion Spectrometer (NAIS): small, intermediate and large ions:

Papers I, III, V use the Neutral cluster and Air Ion Spectrometer (NAIS; Ariel Ltd.; Mirme et al. 2007; Gagné et al. 2011; Mirme and Mirme 2013; Manninen et al. 2016). The NAIS consists of two independent DMAs, one for each polarity. The body of the DMA consists of 21 collector electrodes that measure the current and classify ions according to

their electrical mobility. Additionally, each DMA includes an ion filter and corona-needle charger. This enables the instrument to classify both natural ions and artificially charged neutral particles, with a mobility range of 3.2–0.0013 $cm^2\ V^{-1}\ s^{-1}$, equivalent to 0.8–42 nm of mobility diameter. However, it must be noted that total particles below ~2.5 nm are not considered due to the instrument interference from corona-needle induced ions (Manninen et al. 2011, 2016). The NAIS measures both polarities simultaneously, alternating between ion mode and particle mode, in a 5 minute measurement cycle.

Differential Mobility Particle Sizer (DMPS): total particles in nucleation and Aitken modes: Aerosol particle number size distributions between 3 and 1000 nm can be obtained with a DMPS system (Hauke-type DMA; Aalto et al., 2001) and its Condensation Particle Counter (CPC; TSI Inc., McMurry 2000). The mobility diameter cut-off of the DMPS starts from 3 nm (**Paper I-III**) or slightly higher at 6 nm (**Paper V**). The complete particle number-size distribution was measured in a 10-minute cycle.

Balanced Scanning Mobility Analyzer (BSMA): small and intermediate ions: In **Paper IV** the Balancing Scanning Mobility Analyser (BSMA, Tammet 2006) was used to measure ions with a mobility range of 3.2–0.032 $cm^2\ V^{-1}\ s^{-1}$, or 0.8–8 nm in diameter. The BSMA is built from a two plate DMA connected to a single electrometer measuring at a 10-min time resolution. Unlike the NAIS, the BSMA scans alternating between the positive and negative ions, and only scans naturally charged ions. The size range is limited to under 8 nm compared to 40 nm in the NAIS, but because of its high flow rate (2400 L min-1) the BSMA long-term ion number concentration time series is very consistent.

Particle Size Magnifier (PSM): total sub-3nm particles: NAIS had been exclusively used to reach charged aerosol sizes starting at 1 nm prior to the creation of the Particle Size Magnifier (PSM, Airmodus A09; Vanhanen et al. 2011; Kangasluoma and Kontkanen 2017). With the advent of the PSM, it became possible to detect and measure the concentration of total and neutral (with an ion trap) particles down to 1 nm in diameter, and thereby capture the onset of nucleation. The PSM is a mixing-type condensation particle counter (CPC) where the aerosol sample is turbulently mixed in heated air saturated with a working fluid, like diethylene glycol (DEG). Total sub-3nm particle concentrations were obtained with the PSM in **Paper V**.

3.2.2. Ancillary data

Back trajectories (BT) were calculated to investigate the direction of the air mass reaching the measurement site and the time the air parcel spends over a land or water surface, like the boreal forest in our case. We used the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (Draxler and Hess 1998) and looked at 96-h BT (Tunved et al. 2006; **Paper I**), ultimately selecting the trajectories from clean Arctic air with 90% time spent travelling over land (Sogacheva et al. 2008; **Paper II**).

Meteorology and trace gases**:** The SMEAR II station measures atmospheric gas concentrations, radiation, meteorological variables, among its many soil-forest-atmosphere flux measurements. A mast has continuously measured trace gas concentrations (eg. NOx, SO2, O3, and H2O), eddy fluxes, meteorological parameters (eg. radiation, temperature, RH, wind direction, etc.) from ground level (4 m) to 74 m height until 2011, before expanding to its current height of 125 m (Kulmala et al. 2001). The heights used in this study are 67.2 m (**Paper II**), and inside forest levels of 4 m and 8 m (**Papers I, IV**).

3.3. Data analysis: quantifying new particle formation

3.3.1. Classification of unconventional events

In **Papers II-V** we developed new classification systems where we include features from the ion and particle number size distribution plots that are not part of the Dal Maso et al. (2005) scheme. Table 1 summarizes the main characteristics of each new class, and Fig. 5 presents visual examples of the main classes included in this thesis. Definitions of nonevent, missing data and conventional NPF classes are omitted from this explanation.

Undefined events: Eleven years of data (1996-2006) from SMEAR II aerosol number-size distribution included ~40% of "undefined days" in its classification (see Section 2.2). **Paper II** reclassified the undefined days into a set of new classes: the failed events (with a subset of *tail events* and *quasi events*), pollution peaks, ultrafine mode peaks, and the unclassified. Specifically, the *failed events* class served as an attempt to pick out days that clearly were more related to NPF events than not, so they could be used in further analysis rather than discard them. See Table 1 for summary of the class criteria.

Automated classification – transported events, regional events and ion burst: In **Paper I** the NAIS dataset was used to develop an automated algorithm to re-classify all data into regional events, transported events, ion bursts and nonevents. The transported events and

ion bursts are analogous to the failed events group of tail events and quasi-events from **Paper II**. The classification is based on identifying ion concentration increases at different size ranges of the nucleation mode between 2-25 nm, under the specified time window of 06:00-19:00 local time. See Table 1 for summary of the class criteria.

Nocturnal events: Hirsikko et al. (2007) built up on the traditional NPF classification to include sub-3 nm clustering features visible from the ion spectrometer data from Hyytiälä, Finland. Later, Leino et al. (2016) classified NPF events by defining concentration thresholds for the nucleation relevant size range of 2-7 nm ions using an ion spectrometer (NAIS, see Methods). **Paper IV** used a similar method to identify nocturnal clustering from 11 years (2003-2013) of sub-7 nm ion data. See Table 1 for summary of the class criteria.

Rain events: Rain events have been reported in the literature (Hõrrak et al. 2006; Vana et al. 2008; Tammet et al. 2009; Hirsikko et al 2011), and have shown to increase intermediate ion concentrations, particularly in the negative polarity. Strong burst of ion concentrations in both polarities but enhanced in the negative were observed to appear with the onset of precipitation. See Table 1 for summary of the class criteria.

Table 1: Summary of characteristics for the classification schemes and new events presented in this thesis for **Papers II-V**.

Class	Instrument	Classification characteristics
PAPER II	DMPS	**Undefined days**
Failed events a. Quasi events b. Tail events		a. A new nucleation mode at geometric particle diameters 3–10 nm, but the mode fails to achieve clear growth, the mode lasts for <1 hr, or both. b. A new mode appears at particle diameters >10 nm and grows for several hours.
Pollution-related concentration peaks		Peaks in particle concentration coinciding with elevated concentrations of SO_2 (>1 ppb) or NO_x (>5 ppb).
Ultrafine-mode peaks a. Aitken-mode peaks b. Nucleation-mode peaks		a. Particles appear at sizes between 10-100 nm, but do not grow. Low concentrations of SO_2 (<1 ppb) and NO_x (<5 ppb). b. Particles appear at sizes between 3-30 nm, but do not grow. Low concentrations of SO_2 (<1 ppb) and NO_x (<5 ppb).
PAPER III	NAIS	**Automated NPF classification**
Regional events		A mode including 2-4 nm and 7-25 nm ions is present, and lasts for >1.5hr in the NAIS surface plot.
Transported events		A mode appears at 7-25 nm ions but does not reach down to 2-4 nm. It lasts for >1.5hr.
Ion bursts		A mode including 2-4 nm ions is present but does not reach up to 7-25 nm. It lasts for >1hr.
PAPER IV	BSMA	**Nocturnal clusters**
Sub-3 nm nocturnal event (nighttime)		Concentration of 0.9–3 nm ions increases distinctly during evening/night hours (~17:00–06:00) and/or a 'bump' or a new mode is seen.
Cluster event (CE) (nighttime)		No rain was observed after 15:00 hrs (local time). Concentration of 2–3 nm ions increases during 18:00–24:00 in a sub-3 nm nocturnal event day (previous class). The 2–3 nm ion concentration reaches ≥70 cm^{-3} threshold. A clear bump is seen.
CE nonevent (nighttime)		Concentration of sub-3 nm ions remains low and unchanging throughout the night (~17:00–06:00).
Filtered NPF event (daytime)		NPF event classified as per Dal Maso *et al.* (2005; DMPS data), in which the 2–3 nm ion concentration reaches ≥70 cm^{-3} during 08:00–12:00.
PAPER V	NAIS	**Amazon rain events**
Rain events		Ion concentration burst coincident with the onset of precipitation. If multiple rain events are present in 1 same day, a separate rain event was classified if >1h had passed after the end of the first rain event.

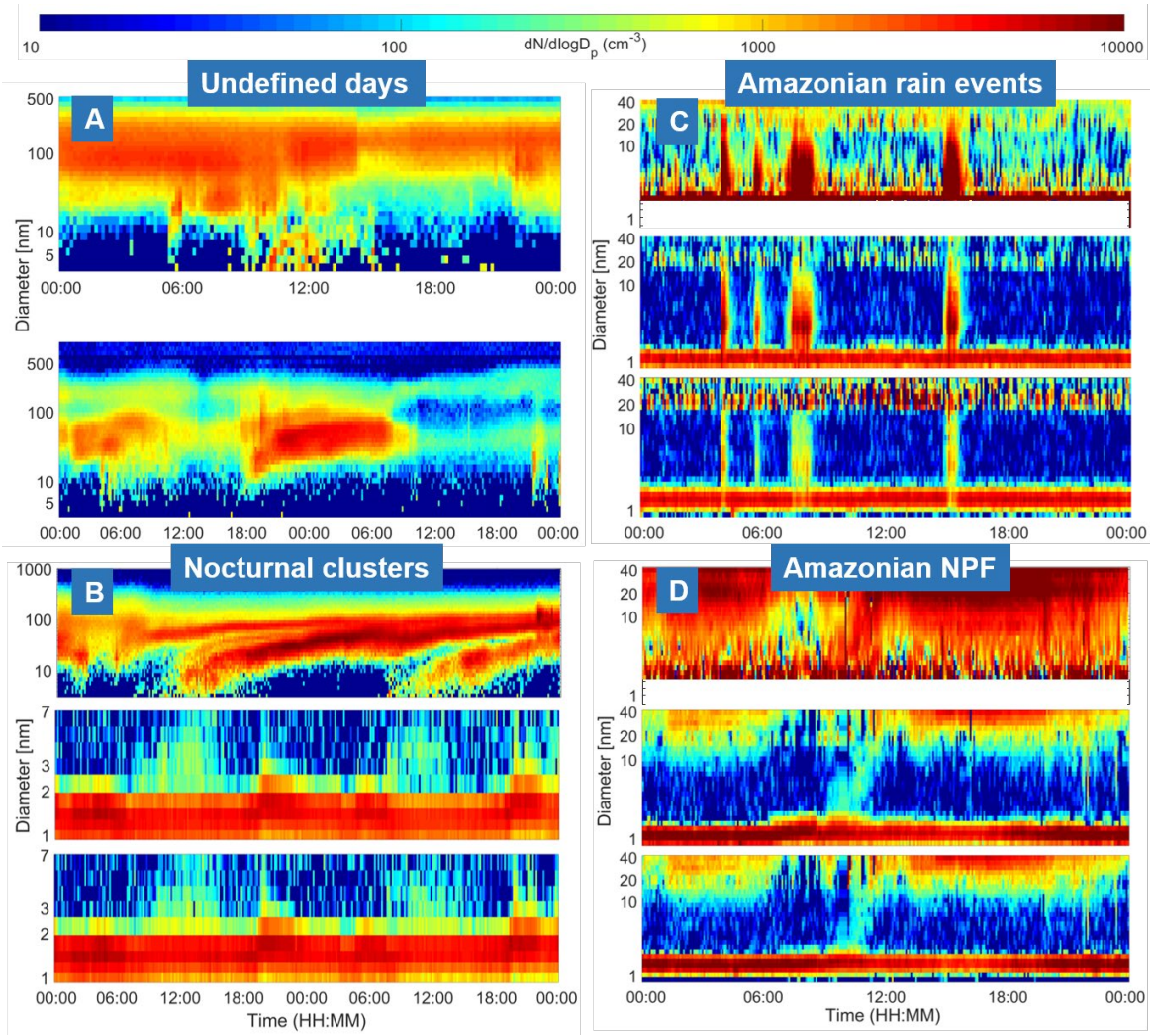

Figure 5: Number-size distribution surface plots for the main classes we have introduced in this thesis. (A) Two previously undefined days re-classified as "failed events" (Top: quasi event. Bottom: tail event) (DMPS data). (B) Nocturnal cluster events (note this surface plot spans 48-hrs, with midnight in the center showing NPF events on the day before and after; BSMA data). (C) Amazon rain-induced ion bursts inside the rainforest canopy and (D) the first observations of NPF in the Amazon Basin at a grassland site. Note: plots B-D consist of total particles (top), negative ions (middle) and positive ion modes (bottom) using the NAIS instrument (C-D, and DMPS (for B top).

3.3.2. Formation of new particles

When nucleation occurs, we can characterize the NPF event by calculating the formation rate of the particle at its diameter, Dp. Note that a formation rate of the smallest cluster ~1.5 nm can be considered the nucleation rate, but beyond this size, we refer to *formation rate* of particles J_{Dp}, where Dp can be, for example, 2-3 nm. We used both the formation rate of neutral particles and ions in the Amazon for **Paper V**, and in our analysis of

nocturnal intermediate ions in **Paper IV.** The formation rate of atmospheric particles (J_{Dp}) (**Paper V**), where D_p is the aerosol diameter in nm, can be calculated from:

$$J_{Dp} = \frac{dN_{Dp-Dp+1}}{dt} + CoagS_{Dp-Dp+} \times N_{Dp-Dp+1} + \frac{GR_{>Dp+1}}{\Delta Dp} \times N_{Dp-Dp+1} \quad (3.1)$$

where $N_{Dp\text{-}Dp+1}$ is the particle concentration between the diameters *Dp* and *Dp+1*, CoagS is the *coagulation sink,* or the rate at which particles of size D_p are lost to pre-existing particles, $GR_{>Dp+1}$ is the rate at which the D_p size particle grow into a larger diameter size bin.

To calculate the ion formation rate (**Paper IV**), that is, the formation of charged particles, we must add additional process that occur between attracting opposite polarity ions (*ion-ion recombination)* and ions sticking to a neutral molecule, thereby charging them (*ion-neutral attachment*). Ion formation rate ($J_i^{\pm}$) is given by:

$$J_{Dp}^{\pm} = \frac{dN_{Dp-Dp+1}^{\pm}}{dt} + CoagS_{Dp-Dp+1} \times N_{Dp-Dp+1}^{\pm} + \frac{GR_{>Dp+1}}{\Delta Dp} \times N_{Dp-Dp+1}^{\pm} + \alpha N_{Dp-Dp+1}^{\pm} N_{<Dp+1}^{\mp} - \beta N_{Dp-Dp+1} N_{<Dp}^{\pm} \quad (3.2)$$

where $N_{Dp\text{-}Dp+1}^{\pm}$ is the ion concentration (in + positive or – negative polarity), α is the ion-ion recombination coefficient and β is the ion-neutral attachment coefficient assumed to be 1.6×10^{-6} cm^3 s^{-1} and 0.01×10^{-6} cm^3 s^{-1} in Hyytiälä conditions, respectively (Israël 1970), and $N_{<Dp+1}^{\mp}$ is the opposite polarity ion concentration at sizes smaller than Dp.

The cloudiness parameter (*P*) is the ratio of measured global radiation (*R*d) to the theoretical global radiation (*R*g):

$$P = \frac{Rd}{Rg} \quad (3.3)$$

where *R*g is dependent on latitude and day of the year. We used $P > 0.7$ to determine clear-sky conditions in **Paper I** (Perez et al. 1990; Sogacheva et al. 2008; Sánchez et al. 2012).

4. Results and discussion

4.1. NPF needs sunlight, clear skies, and clean air in a boreal forest

During an eclipse seen at SMEAR II station, an NPF event was abruptly interrupted; at the same time sulfuric acid concentration dropped, only to resume once the solar event was over (Jokinen et al. 2018). This example highlights the importance of solar radiation for NPF in Hyytiälä, Finland. Other studies have concurred that solar radiation, and in particular a clear sky, is one of the key markers of NPF events (Birmili and Wiedensohler 2000; Hyvönen et al. 2005; Sogacheva et al. 2008; Baranizadeh et al. 2014; Gröss et al. 2018; Nieminen et al. 2018; Kerminen et al. 2018; **Paper I**). A clear sky maximizes the intensity of incoming solar radiation that is needed for photochemical reactions to produce sulfuric acid from its precursor gases (such as fossil fuel emissions and algal dimethyl sulfide).

In **Paper I,** we looked at the past 20 years (1996-2016) of ambient data from SMEAR II station and defined a clear sky day as one with a cloudiness parameter of $P > 0.7$, that is when measured UV radiation is 70% of what is theoretically expected for the day. We find a clear distinction between median P values of NPF events (median $P = 0.75$) and nonevents (median $P = 0.25$). Undefined days had intermediate P values, as is the case for most other NPF-determining conditions (**Paper II**). Cloudiness (or the P value) is therefore an effective parameter to discern between the classes. There remained however a small percentage of nonevent days (~15%) that occurred during sunny, clear sky conditions, and it was most informative to investigate these cases further. On these days, condensation sink (CS) was found to be next determining factor, as has been previously acknowledged in data mining techniques for Hyytiälä (Hyvönen et al. 2005). We were able to parameterize a CS threshold that grouped the majority of the clear sky nonevents (~95%) (**Paper I** Eqn. 6 therein) as a function of temperature. We must highlight however, that this efficiency of CS to segregate nonevents from NPF worked only during the spring season. This no longer applied in the remaining seasons. We looked at the probability of NPF event based on the CS and T values and found that high CS deters NPF in Hyytiälä with no effect from T. At low CS, the probabilities of NPF increased at warmer temperatures, pointing to warm, sunny days with clean air conditions. High temperatures, however, would decrease the number of NPF days, possibly relating to higher evaporations of the initial clusters. Additionally, air masses during clear sky NPF were on average from

northwesterly direction compared to southerly for nonevents, as expected for SMEAR II station (Nieminen et al. 2014; Sogacheva et al. 2008). Overall, solar radiation during clear skies seems to be the most determining parameter for NPF events, followed by CS, in Hyytiälä, Finland.

4.2. Defining undefined days: a case of advected or interrupted NPF

Having established that clear sunny skies and low background aerosol concentration (CS) are most favorable parameters for NPF in Hyytiälä, we aim to take a step further by looking at the days where some characteristic of NPF was present, but remained too ambiguous to be classified as such: namely, the "undefined days" class.

An NPF event is conventionally identified in field observations by using the classification of Dal Maso et al. (2005). Days in Hyytiälä are classified as either NPF events of Class Ia, Class Ib, Class II, nonevents or left as undefined (see Fig. 2 for examples of these classes). The fraction of NPF events ranges from approximately 10% to 50% from winter minimum to summer maximum (Nieminen et al. 2018), but a hefty fraction (~40%) of the dataset is discarded as undefined. In **Paper II**, we re-evaluated eleven years (1996–2006) of undefined days (1630 days) and subdivided them into three new classes (see Table 1 in the Methods section): failed events (37% of all previously undefined days), ultrafine-mode concentration peaks (34%), and pollution-related concentration peaks (19%), with a mere 10% left as unclassified. Previously, Hirsikko et al. (2007) adapted the Dal Maso et al. (2005) classification to fit the BSMA ion spectrometer instrument that narrows the dimeter range to 0.8-7.5 nm. Specifically, they included a class of ion burst events that did not grow past 5 nm (class Ib1), and a second class (class Ib2) where there was a gap in between the cluster ion band (<2 nm) and the larger sizes. What is interesting is that following an instrumental limitation and adaptation, Hirsikko et al. (2007) identified possible indications of ion-induced bursts (class Ib1) and a neutral-pathway dominated burst (class Ib2) that would not have been noticeable using a DMPS, and therefore are not included in the conventional classification of NPF days. We identified a similar characteristic from the DMPS data as a sub-class of the failed-events, one that we refer to as *quasi-events* in **Paper II** (16% of previously undefined days,), and later on as the *ion burst* class (**Paper III**) and nocturnal nanoclusters (**Paper IV**) using NAIS data, all a case of small and intermediate ions that do not grow or last long (<1 h), and are therefore not classified as per Dal Maso et al. (2005). We can make an analogy with the 'bump' events

that have also been observed in coastal Mace Head (Vana et al. 2008; Manninen et al. 2010), and that are related to intense iodine-nucleation (O'Dowd et al. 2002; Sipilä et al. 2016).

The failed events included the *tail events* (21% of previously undefined days), featuring growing particles in the Aitken sized mode (>25 nm), which we interpreted as NPF events that began elsewhere and were advected to Hyytiälä at a later stage of their growth. This phenomenon has been seen in various environments as growing modes in the number-size distribution plot (Kyrö et al. 2013; Chen et al. 2017; Cai et al. 2018) or in a vertical profile with a high concentration of nucleation mode particles observed at an elevated altitude which could be brought down by convection (Wang et al. 2016b; Andreae et al. 2018; Lampilahti in prep). We can suggest that tail events are new particles transported from a higher altitude or horizontally from a non-regional NPF. Following the classification presented in **Paper III**, both advected (*transported events*) and truncated (*ion bursts*) events are accounted for (see Section 4.3).

In terms of intermediate environmental conditions, the failed events class were most numerous during summer and accounted for the Hyytiälä summer dip in NPF frequency, between the NPF maxima in spring and fall (**Paper II**, Fig. 5 therein). Overall, boreal regions have reported the same NPF event seasonality, with a maximum in spring and fall, and the summer dip in between (Manninen et al. 2010; Kyrö et al. 2013; Vana et al. 2016; Nieminen et al. 2018). It must be noted that it is during the summer months when we observe the highest growth rates (GR; Nieminen et al. 2014, 2018) and concentrations of organic vapours (eg. monoterpenes, Peräkylä et al. 2014) in Hyytiälä, as well as high boundary layer turbulence due to the warmer temperatures. Could we be considering a seasonality based on the horizontally homogenous regional NPF cases (Hussein et al. 2009; Crippa and Pryor 2016), and neglecting to include in our analysis NPF cases possibly advected from higher altitudes?

Referring back to environmental parameters favoring NPF in Section 2.3 (Hyvönen et al. 2005), the failed events class presented CS and global radiation values in-between those of event and nonevent days, although overlapping more with event CS values (**Paper II**, Fig. 8 therein). A 96-h back trajectory of particle-size concentrations as a function of time spent over land for the failed event class displayed a similar growing banana as the event class (albeit starting at a larger size *Dp*), indicating a clean air mass from the direction of the Arctic Ocean, collecting organics over land with which to grow.

We can determine thresholds to constrain particle formation events, but these will serve as indicators to days with a higher probability of being a regional NPF event, such as the values of CS, RH, or cloudiness parameter, as we discussed in the section before (**Paper I**). However, to achieve a more representative approach to quantify secondary aerosol number concentration, we should integrate into our analysis the discarded undefined class, which is important to keep in mind is almost half of the data available in Hyytiälä. We could consider how the presence of failed-event cases influence the remaining aerosol population – as Hirsikko et al. (2007) speculated on the ion/neutral pathways based on their new classification— and more specifically look deeper into which factors promote or inhibit their full range growth (Paasonen et al. 2018). We next introduce a classification that extends the current classification of Dal Maso et al. (2005) with ion burst, advected cases, and furthermore, is automated (**Paper III**).

4.3. Extending the NPF classification: burst and transported events included

Following a successful re-classificaiton of 37% of undefined days into a *failed-event* class, we developed an automated classification method using the NAIS ion and particle mode using 10 years of ground observations at SMEAR II, Hyytiälä (**Paper III**). It considers conventional NPF characteristics (as Dal Maso et al. 2005) as well as includes the failed events classification from **Paper II**. Specifically, similar to Hirsikko et al. (2007), sub-3nm sizes are incorporated into the classification by making use of the NAIS ion mode. From the full 10-year dataset, 18% of the days resulted in ion bursts that failed to grow. Transported NPF events (*tail events* in **Paper II**) made up 17% of the days. Regional NPF events constituted 24% of our 10-year data, for which we found the environmental conditions to be clear sky, low CS, consistent with our previous work (**Paper I,II**). It is important to mention that the fraction of regional NPF events observed here is comparable to the percentage obtained for conventional NPF days (23% during 1996-2012 in Nieminen et al. 2014) following the manual and visual classification of by Dal Maso et al. (2005). This result is encouraging. The automated classification facilitates and standardizes the analysis of NPF. Even more, by working on the principle of particle concentration increase, rather than a manual and visual picture of an NPF event plot, we become more flexible to address questions like: what could be causing the increase in the particle number concentration and how much is it adding to the aerosol mode on a particular day that may otherwise have been discarded from analysis? Overall, the automatic

classification allows for a broader study of processes that contribute to increases in nucleation-mode particle concentrations.

4.4. Nighttime ion clusters are a frequent phenomenon in Hyytiälä

After looking at intermediate conditions for NPF, it is reasonable to ask which processes, other than the expected daytime NPF events governed by sulfuric acid could be attempting to form new particles in the boreal atmosphere. Particle formation rates during non-event days themselves are rarely zero but simply low (Riipinen et al. 2007; Kulmala et al. 2013). We could suggest that NPF is not absolutely switched off, but rather it is outcompeted with other processes or environmental conditions. This leads us to examine the next unlikely time for NPF: the nighttime. The evening time window in Hyytiälä has previously shown indications of clustering (Junninen et al. 2008; Lehtipalo et al. 2011). Scarce, yet existing ambient observations indicate that NPF-related processes can occur at nighttime during dark hours (Wiedensohler et al. 1997; Suni et al. 2008; Svenningsson et al. 2008; Kalivitis et al. 2012; Kecorius et al. 2015; Kammer et al. 2018).

Daytime photochemical oxidation is an attributed requirement for NPF (Kerminen et al. 2018; Nieminen et al. 2018), and we have seen that in Hyytiälä in particular, it is the most determining factor (Jokinen et al. 2018; **Paper I**). However, several studies, including dark ozonolysis experiments in the laboratory (Ortega et al. 2012b), have shown a presence of nighttime highly oxidized molecules in Hyytiälä (Ehn et al. 2014; Yan et al. 2016; Bianchi et al. 2017; Zha et al. 2018) and the possibility of purely biogenic nucleation (Kirkby et al. 2016; Bianchi et al. 2016; Lehtipalo et al. 2018; Junninen in prep). In an earlier study Lehtipalo et al. (2011) observed ambient nano-clusters during nighttime in Hyytiälä, which they proceeded to simulate in a flow chamber with the oxidation of organic vapors and found their results agreed with their field observations.. We looked at 11 years of ion data and identified a nocturnal sub-3nm ion burst in a third of the days in our dataset (negative ion = 1324 days, positive ion = 1174 days). In a process similar to Leino et al. (2016), we identified bursts that would be most comparable to daytime NPF-process (see Table 1 in Methods). The selected burst surpassed concentrations of 70 ions cm^{-3} in the size ranges indicative of NPF process: 1.5-2 nm, 2-3 nm, and 3-7 nm (referred to as nighttime *cluster events* from here on; see Table 1). In summary, we found that ~1 – 3 nm clusters form at nighttime in concentrations comparable or surpassing those during daytime NPF events, but they fail to grow thereafter (Fig. 6, taken from Paper III). A very interesting

observation was that the temporal appearance of these nocturnal cluster events mostly followed, or were preceded by, a daytime NPF (~55%) or an undefined day (45%). This indicates a possible common set of conditions or chemistry is shared in both day and nighttime clustering processes.

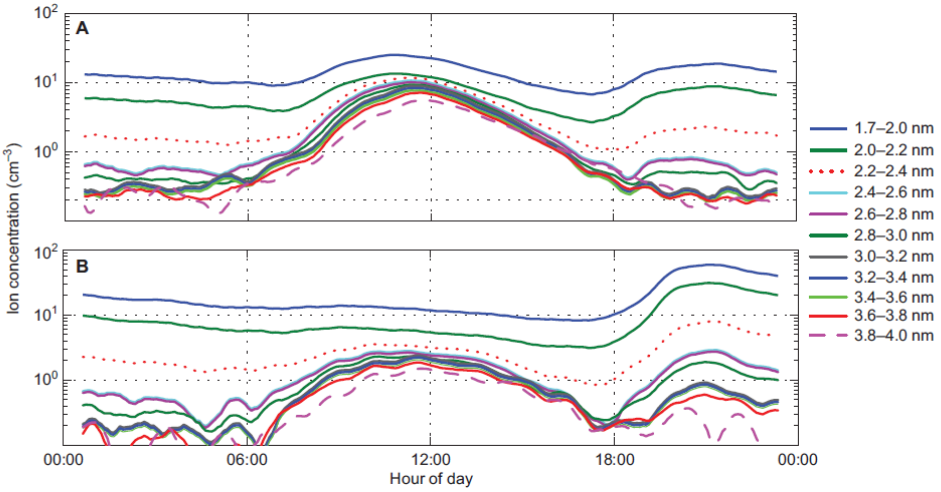

Figure 6: Median diurnal ion concentrations for 1.7 to 4 nm ion size bins for selected* (A) NPF and (B) days presenting a nocturnal cluster event between 18:00-0:00. *Both NPF days and nocturnal cluster events selected in this study presented ion concentrations ≥70 ion/cm-3 during their respective event hours (08:00-12:00 for NPF events, 18:00-00:00 for nighttime cluster events).

Following this study, Rose et al. (2018) compared the cluster events identified in Paper IV to HOMs concentrations and found that the formation rate $J_{1.5}$ of the bursts correlated with HOMs dimers, in the absence of sulfuric acid, indicating ion-induced biogenic nucleation.

While the nocturnal nano-clusters did not appear to grow, it is important to highlight that a new and frequent (one third of days) pathway for cluster formation was established in Hyytiälä SMEAR II station. This pathway should be investigated in more detail and in other sites. For example, we are looking for similar HOM's clustering in ion data from ground versus above canopy heights specifically during nights with an inversion layer (Zha et al. 2018; Chen et al. 2018; Buenrostro Mazon in prep).

Nocturnal events have shown to grow across the full nucleation-mode size range in some environments (Suni et al. 2008; Kammer et al. 2018, Junninen et al. in prep.), and therefore their possible contribution to the regional aerosol population should be investigated. Additionally, as was the case with Rose et al. (2018), looking at this peculiar phenomenon

led to a confirmation of a new nucleation pathway in the long-term monitoring SMEAR II station. This, once again, reinforces the need to analysis as much of the dataset as possible, to account for new processes and particle sources.

4.5. First-time observations of ground-level NPF in the Amazon

Finally, we compared a long-term time series of nucleation mode aerosols inside the Amazon rainforest to that at an open pasture site in the Amazonian capital, Manaus. We observed the first evidence of NPF at ground level in the Amazon at the pasture site (site T3), although no NPF events were observed inside the rainforest.

The Amazon rainforest is an extremely diverse ecosystem and it is often under pristine conditions unperturbed from anthropogenic pollution (Martin et al. 2010, 2017; Andreae et al. 2015). But it is also a forest rich in isoprene (Gu et al. 2017) with the ratio of isoprene to monoterpene being typically >10 (Greenberg et al. 2004). The sulfuric acid concentration in Amazon is lower by a magnitude compared to concentrations measured in Hyytiälä, or in an isoprene-forest in the US (Kanawade et al. 2011). Isoprene has been shown to inhibit secondary aerosol formation by scavenging oxidants (McFiggans et al. 2019) that would otherwise oxidize more favorable NPF precursors like monoterpenes (Kiendler-Scharr et al. 2009; Lee et al. 2016). However, NPF observations in other rainforests (Suni et al. 2008, Tumbarumba, Australia) or isoprene-rich forest (Yu et al. 2014) have been observed.

In the Amazon, NPF has been reported to begin in cloud outflows following cloud processing in the free troposphere (FT) after which the nucleation mode particles are rapidly transported to the ground where they are observed as particles a few nanometers in size (Zhou et al. 2002; Wang et al. 2016b). In our data, no indications of NPF were observed inside the rainforest canopy during our two-year time series. We did identify rain events that enhanced intermediate ion concentrations substantially, reaching concentrations of 10^4 cm^{-3} and lasting up to several hours. What is also interesting is when we compared a few available days of data from the neighboring ATTO tower's DMPS, we could only see the strong enhancement of rain-induced intermediate ion concentrations inside the canopy (see Fig. 5). More importantly, there seems to be a growing nucleation mode prior to the rain in the tower DMPS data (a *transported event* under the **Paper II/III** classification, possibly from a higher elevation in the troposphere), but this is not observed in the NAIS at ground level. The shielding effect of the canopy, and more interestingly, the enhancement

of rain-produced intermediate ions inside the canopy and not above it has also been observed in SMEAR II, Hyytiälä between ground and above canopy tower measurements (35 m height; Buenrostro Mazon in prep.). These examples point to (1) the need to further investigate the effect of a forest canopy on nucleation mode concentrations, and (2) to the discrepancy in vertical observations seen between ground level and tower measurements, in particular due to a canopy in between. This is most important when generalizing our ground station measurements to represent the overall boundary layer, and should be considered in the future planning of new stations.

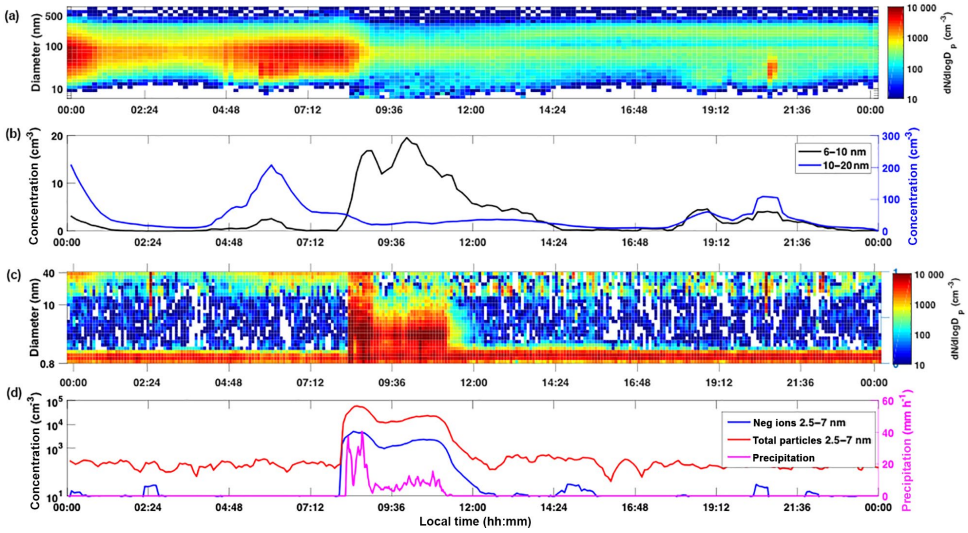

Figure 7: Aerosol and ion data for the Amazon rainforest site T0t (see Methods). (a) Number size distribution surface plots and (b) 6-10 and 10-20 nm particle concentrations, from a DMPS instrument located at a 60 m height tower. (c) Inside canopy ground-level NAIS surface plot and (d) its intermediate ion (2.5 - 7 nm) and rain concentrations.

New particle formation was observed for the first time at ground level in the Amazon pasture site (see ion and total particle surface plots in Fig. 5) on 5% of days. While clearly grassland and rainforest sites are not intercomparable environments (Fisch et al. 2004) nor were they directly adjacent to one another, it reiterates the importance of carrying out field observations in as many representations of biomes in different geographical locations as possible. In this case, literature reports that no NPF is observed in the Amazon rainforest, but we have now shown NPF in the Amazon grassland. This is particularly interesting as land-use change in the Amazon is specifically transforming the landscape from rainforest to grasslands. The main results of **Papers I-V** are summarized in Table 2.

Table 2: Summary of the environmental conditions present during the alternative classes studied in this thesis. The frequency and main characteristics of undefined days and nocturnal clusters events in Hyytiälä, Finland, and NPF at ground level in an Amazon grassland. Note that temperature (T), relative humidity (RH), and condensation sink (CS) values are for Spring only, except for the Amazon site, where NPF occurred only in the Austral summer (Jan-Mar; wet season). In the case where the same event type is studied in multiple papers, the corresponding value to the respective paper is indicated by a superscript letter *a* or *b*. P = cloudiness parameter (see methods Section 3.3.2).

Event type	Frequency	Spring T (℃)	Solar radiation	Spring CS (s^{-1})	Spring RH	Season peak	Notes
NPF in Hyytiälä (Nieminen et al. 2014, 2015[a])	23%	11[a]	High	2.2. x10^{-3}	45%[a]	Spring /fall	J_{3-25} = 0.84 $cm^{-3}s^{-1}$, GR_{3-25} = 2.5 nm h^{-1}
Paper II[b]/III							
Regional event	24%	4	High (P= ~0.8)	1.7 x10^{-3}	58%	-	
Transported (*Tail event*[b])	17% (*16%*)[b]	5	Medium (P= ~0.5)	3.0 x10^{-3}	76%	Summer[b]	
Ion burst (*Quasi event*[b])	18% (*21%*)[b]	1.5	Medium (P= ~0.4)	2.5 x10^{-3}	79%	Summer[b]	
Nonevents	41%	3	Low (P= ~0.3)	3.1 x10^{-3}	86%	Winter	Nonevents as classified according to Paper III
Paper IV Nocturnal clusters	26%	10	--	2.3 x10^{-3}	45%	Spring	90% occur on days classified as NPF (55%) or undefined (35%)
Paper V NPF in Amazon	5%	26	High	1.8 x10^{-3}	90%	Austral summer (wet season)	J_{3-7} = 0.25 $cm^{-3}s^{-1}$ GR_{3-7}= 13.3nmh^{-1}

5. Review of papers and author's contribution

The SMEAR II station in Hyytiälä, Finland (Hari and Kulmala 2005) has the world's longest aerosol number size distribution dataset and can serve as a reference for atmospheric aerosol research in a rural environment. The essentiality of sunlight for NPF was demonstrated in **Paper I**, where we studied the effect of cloudiness on NPF. From previous studies we know that solar radiation is a determining parameter in enabling NPF . In this paper we looked at the small fraction of nonevent days (~15%) that occurred on sunny, clear sky conditions, and by comparing them to sunny days with NPF, we identified that in addition to sunlight, the NPF days had a higher concentration of volatile organic compounds, lower condensation sink and lower ambient temperature. We derived an equation to parameterize the NPF-favorable conditions from CS and T variables. I assisted and co-supervised the preliminary results of this research, contributed in discussion and finalization of the paper.

New particle formation events are frequent in SMEAR II (~23% annually, Nieminen et al 2014; up to 50% of days in spring, Nieminen et al. 2018). However, approximately ~40% of the data was previously classified as *undefined*. **Paper II** focuses on this discarded dataset under the logic that by looking at days which present some favorable conditions, but not all, we are able to highlight which parameters are most crucial for NPF in this location. The values of relative humidity, temperature and condensation sink on *failed events* (37% of undefined days) presented intermediate values between the NPF events and nonevents days, with a higher overlap with NPF values. I conducted the majority of the data analysis and wrote most of the paper.

Identifying NPF events is traditionally done manually following a visual inspection protocol outlined by Dal Maso et al. (2005; see Kulmala et al. 2008). This leads to a time-consuming effort and to ambiguity in the decision-making process where days are simply put in the undefined-days category. To alleviate both concerns, in **Paper III** we propose an automated classification scheme that is based on increases in ion or particles in the nucleation mode beginning at 2 nm. This allows the inclusion of ion bursts and non-regional NPF characteristics. I participated in processing the ion data, the discussion of the results and editing of manuscript.

While we established that the clear sunny days are a perquisite for successful NPF, earlier laboratory experiments showed oxidation leading to NPF to be possible without the photochemistry from sunlight through, for example, dark ozonolysis (Ortega et al. 2012b; Boulon et al. 2013). **Paper IV** presents 11 years of nighttime ion data in Hyytiälä and demonstrates that nocturnal (18:00-00:00 hours) ion clusters grow beyond the cluster-band pool range and occurs frequently in the boreal forest environment (~30% of days). Enhanced 1.5 to 2 nm ion concentrations at night surpassed the daytime ion concentration in the same size range during conventional daytime NPF events by more than a factor of 2. However, no growth of nocturnal ion clusters outside the intermediate size range of ~2.4–7 nm was observed, and the intermediate ion concentrations remained lower than those during daytime NPF events. We conclude that the nighttime forest is a source of sub-3 nm clusters that fail to grow, probably due to insufficient amounts of highly oxidized vapors to support the growth. I conducted the analysis and the writing of the paper.

Nucleation mode particles have been detected at ground-level height in the Amazon starting at sizes around ~20 nm, where the formation of the particles is suggested to begin in the cloud outflows and transported vertically with high velocity downdrafts (Zhou et al. 2002; Wang et al. 2016). **Paper V** is the first study to show ultrafine mode particles down to 2 nm and the start of new particle formation events at ground level in the Amazon basin. Two sites were compared: an open pasture site where new particle formation events were observed in 8 of 64 days of an intensive campaign period, and a rainforest site where the predominant feature was rain-enhanced intermediate ions bursts. NPF had been observed to occur practically all over the world except the Amazon region. With this study we introduce the first NPF characteristics, including the formation and growth rates of new particles formed in an Amazon grassland, 70 km west from the Amazonian city of Manaus. In this study, I analysed the long-term data set of the rainforest site (site T0t), performed the analysis for site T0t, and co-wrote the site's section in the paper.

6. Conclusions

Figure 8: Schematic summary of the results in Paper I-V. Paper I on the determining effect of clear sky conditions for NPF. Paper II,III on accounting for non-regional NPF events or transported events as observed from a ground station (pink shade).). **Paper IV** on nocturnal clustering events outside typical NPF time window. **Paper V** on the first observations of NPF at ground level site in the Amazon, and the production rain-induced intermediate ions inside a forest canopy.

A summary of findings from Paper I to V

Figure 8 summarizes the work in this thesis, which focused on the following aspects: (1) We determined the indispensible environmental conditions needed for NPF in a boreal forest, namely cloudless sunny days, with low background aerosol concentrations (low CS), intermediate temperatures, and low RH complemented by higher concentrations of oxidized organics (**Paper I**). (2) We identified cases where previously undefined days could be re-explained as NPF events that began at higher altitudes and were brought down or advected to SMEAR II at sizes above nucleation mode, or when NPF was truncated early on (**Paper II**). We incorporated these findings to develop a new automated classification that accounts for sub-3 nm ions with the NAIS ion mode data and complements it with NAIS particle-mode data to retain the regional NPF features described by Dal Maso et al. (2005) (**Paper III**). (3) We explored nighttime clustering in Hyytiälä, which was observed frequently (~30% of nights) in the boreal forest under conditions likely with insufficient material to allow growth beyond ~3 nm (**Paper IV**). Nocturnal clustering commonly preceeded or followed a day-time NPF, suggesting common

conditions that favor clustering. Additionally, there was a clear distinction in behaviour between small ions and NPF-relevant ions sizes: cluster ion concentrations remained in the same order of magnitude across night and day, events and nonevents. Intermediate ion concentrations in the 3-7 nm range were only elevated during NPF events. However, ions between 1.5-3 nm were comprably elevated during noctural clustering and NPF events, suggesting that nocturnal clustering is as effective as daytime clustering in Hyytiälä, but the clusters fail to grow and instead are lost during the course of the night. In a follow-up study, the nocturnal events in **Paper V** were identified as ion-induced clusters from HOMs (Rose et al. 2018). Therefore, we have identified a new pathway of cluster formation in Hyytiälä, Finland. (4) Rain as a source of intermediate ions was observed within the Amazon rainforest canopy (**Paper V**). This effect was not observed in the tower measurements ~60 m above the rainforest floor, indicating that rain induces an ionising mechanism inside a forest canopy, which is also observed inside the forest canopy of boreal Hyytiälä, Finland (Buenrostro Mazon in prep.). (5) While no NPF was observed inside the Amazon rainforest from a 2-year dataset, we report ground-level NPF events on 8 of 64 measurement days at a pasture site in the Amazon for the first time (**Paper V**). This highlights the need to expand our observations and to avoid misrepresenting an area or biome based on spatially-limited monitoring. Additionally, the Amazon has been experiencing dramatic changes in land use, as rainforest is deforested to give way to agriculture and farm lands (Pedlowski et al. 1997; Nobre et al. 2016). The change from forest to grassland makes our findings of NPF in the Amazon particularly relevant.

A case of misfits: for a more robust analysis of NPF processes

We commonly analyse NPF in a binary system of *events* versus *nonevents*. Based on the results of this thesis, we could rather view them as NPF days, versus days with a potential for NPF, even if small, in the same way as we report particle formation rates for nonevents. The atmosphere is never turned off. There is a fluidity in the configuration of conditions leading to NPF, covering from molecular scales to mesoscales in meteorology. The most efficient chemical and ambient configuration leads to NPF, but when those conditions change, the next most favorable mechanism takes over, enriching our fieldwork with a variety of observable features.

Regional level NPF events have been observed in various multi-station, multi-national studies (eg. Manninen et al. 2009; Hussein et al. 2009; Crippa and Pryor 2013; Vana et al.

2016). An NPF event due to the way it is classified (Class I and II in Dal Maso et al. 2005) will most likely be a regional event. From these events we characterize the dynamics and rates of formation, growth and condensable vapour concentrations. This means that our global overview of NPF is characterised and quantified based predominantly on the regional processes we have analysed. This is reasonable when considering our aim to quantify climatically relevant aerosols and to understand the life-time development of an aerosol population, at regional and global scales. Why place importance on a nucleation mode burst that fail to grow, or a night-time cluster that breaks up before the morning boundary layer expands? Not all these cases may not contribute directly to CCN loading, but considering them in the analysis helps us reveal and understand NPF processes better, such as what accounts for the night-time NPF/clusters/burst observed around the world (Kecorius et al. 2015; Kammer et al. 2018; Junninen in prep.). Undefined days, which have been reported at various sites around the world (eg. dos Santos et al. 2015; Nemeth et al. 2018), could be incorporate in NPF-analysis if they show *failed event* type features (eg. Ling et al. 2019). This would be particularly useful in sites where regional NPF observations are scarce, such as the case in Siberia where NPF is infrequent and undefined days are substantially more numerous (Dal Maso et al. 2007, Wiedensohler et al. 2019).

Instrumentation improves with the years. We are now able to see down to the size range of molecules and molecular clusters, and hence to look into the realm of gas-to-particle phase transitions. An NPF classification based on an instrument with a cutoff size of >3 nm can now be updated. Data from ion spectrometers with detection capabilities down to ~1 nm ions have served to efficiently classify days with NPF events (Hirsikko et al. 2007; Leino et al. 2016; **Paper II**). By taking into account the increase in instrumental resolution and expanding the features in the classification of NPF, we can make the analysis of NPF processes more robust.

It would be most interesting to reclassifying the *undefined days* that are prevalent around the world, in order to mine for alternative processes and quantify aerosol concentrations that we may be omitting. By expanding our time-window and size-range during NPF analysis, we can assess the inhomogeneities surrounding a ground, single-point measurement station, particularly as we expand our international networks of stations (Kulmala 2018; Weatherhead et al. 2017, 2018). SMEAR II is a homogenous, boreal forest station with little anthropogenic influences nearby. Yet there are conditions, such as during a shallow boundary layer (Zha et al. 2018; Chen et al. 2018; Buenrostro Mazon in prep.),

when we observe differences in the concentration of trace gases and nucleation mode particles and ions between ground level and at the 30 meter high tower. In addition, Junninen et al. (in prep) have shown that a wetland ~5 km away can have a distinctly different decoupled boundary layer – and hence chemistry— to the boreal forest of SMEAR II.

This thesis compiled research on unconventional NPF-related features, and it can be concluded that omitting these events may lead to oversights of potentially interesting, if not important, processes. Furthermore, the analysis of field observations could incorporate these rarer cases in order to propose new mechanisms or ambient conditions to feed in to experimental set-ups and ultimately into models. This may help account for some of the discrepancies between field observations and models, and better quantify the contribution of NPF to total aerosol loading and climate-relevant nuclei concentrations at a globally representative scale.

To end on a personal note:

During a discussion with artist Josefina Nelimarkka over a cup of coffee, she asked me: what is the color and shape of aerosols? A perfectly good question, not only from an artist, but I can imagine any non-aerosol scientists would be curios to get a mental image of the little nanoparticles that we are able to detect and count, one by one. However as an aerosol scientist, it is easy to assume a perfectly round, solid sphere with density of 1, and then to forget about it once the equation is set. Of course, colleagues of mine literally photograph coarser aerosols with electron microscopes, or play with the stereochemistry of clusters in the computer simulations. However, as someone who is looking at ready conditions when the particles have appeared, I focus on other things. So when I get a question such as Josefina's, I am reminded how we tend to narrow the focus of our work, especially in a PhD, forgetting to contextualize our topic in the larger picture. With an 'easy question' we are reminded that to be experts, we must understand all the scales of our field and further implications across disciplines, particularly in aerosol science where the ramifications of our research extend to human lives and our future environment.

It is those easy questions that made us scientists in the first place. For our own benefit and for science, it does well to maintain that curiosity-filled enthusiasm that fuels our desire to understand the world around us.

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